524184

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁷: G01N 33/00, 27/12

(21) International Application Number:
PCT/GB2003/004322

(22) International Filing Date: 8 October 2003 (08.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0223350.0   8 October 2002 (08.10.2002)   GB

(71) Applicant (for all designated States except US): CITY TECHNOLOGY LIMITED [GB/GB]; City Technology Centre, Walton Road, Portsmouth P06 1SZ (GB).

(72) Inventors; and
(75) Inventors/Applicants (for US only): SMITH, Peter, John [GB/GB]; 127 Rutten Lane, Yarnton, Oxon OX5 1LT (GB). PRATT, Keith, Francis, Edwin [GB/GB]; 22 Roebuck Court, Didcot, Oxon OX11 8UT (GB).

(74) Agent: GILL Jennings & Every; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SOLID STATE SENSOR FOR CARBON MONOXIDE
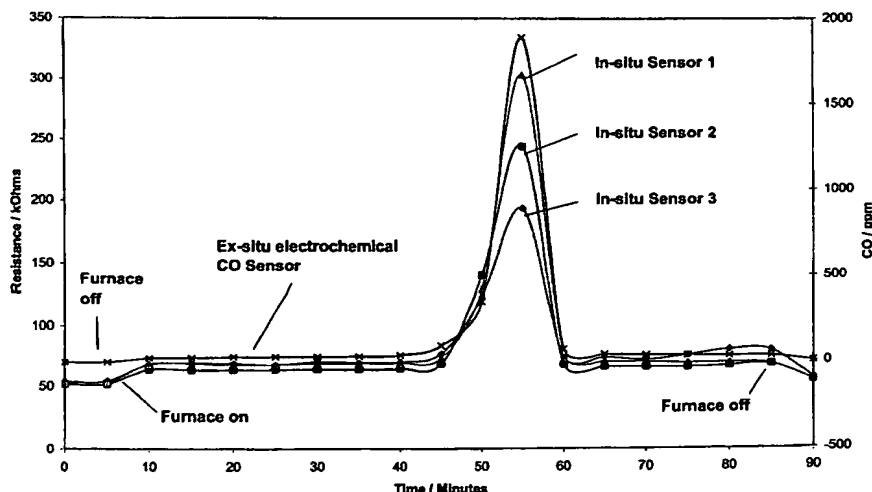
Behaviour of 3 p-type MMOS sensors in a flue atmosphere. The response of an electrochemical CO sensor in a cooled extracted sample of the gas is also shown.

(57) Abstract: A method of detecting a predetermined alarm condition in a combustion emission gas. The method comprises exposing to the gas a semiconductor gas sensor having a p-type mixed metal oxide semiconducting material of the first, second and/or third order transition metal series, the semiconducting material being responsive both to a change in concentration of a reducing gas in the surrounding atmosphere and to a change in concentration of oxygen in the surrounding atmosphere to exhibit a change in its electrical resistance. The resistance is monitored and an alarm signal is output if the resistance exceeds a predetermined value corresponding to the alarm condition.

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference RSJ07615WO	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/GB 03/04322	International filing date *(day/month/year)* 08/10/2003	(Earliest) Priority Date *(day/month/year)* 08/10/2002

Applicant

CITY TECHNOLOGY LIMITED

SOLID STATE SENSOR FOR CARBON MONOXIDE

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of _____4_____ sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

      [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

      [ ] contained in the international application in written form.

      [ ] filed together with the international application in computer readable form.

      [ ] furnished subsequently to this Authority in written form.

      [ ] furnished subsequently to this Authority in computer readble form.

      [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

      [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable (See Box I).**

3. [ ] **Unity of invention is lacking (see Box II).**

4. With regard to the **title,**

   [ ] the text is approved as submitted by the applicant.

   [X] the text has been established by this Authority to read as follows:

   SOLID STATE SENSOR FOR CARBON MONOXIDE

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.   6

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [X] because this figure better characterizes the invention.

   [ ] None of the figures.

SOLID STATE SENSOR FOR CARBON MONOXIDE

The invention relates to a method and system for detecting a predetermined alarm condition in a combustion
5   emission gas.

Concern over the generation of dangerous levels of CO by malfunctioning or incorrectly adjusted domestic gas appliances has been rising in recent years. To comply with current ANSI standards in the US and ever increasing
10   constraints on CO_2 emissions in the EU, there is an increasing interest in combustion or flue monitoring technology.

Flue gas atmospheres represent particularly aggressive conditions. Temperatures range from 40°C to 200°C
15   (depending on the degree of cooling by the heat exchanger and whether or not the furnace is of a non-condensing or condensing design) while the gas itself is saturated with water vapour and creates reducing conditions due to low overall oxygen levels, typically ~ 5%. Other components
20   are CO_2 and CO, typically at around 8% and 30ppm respectively, with the balance being predominantly nitrogen. In the event of the flue being restricted, or of the air/fuel pre-mix not being correct, the O_2 level in the flue decreases. The CO level remains unchanged until the
25   system becomes fuel-rich, whereupon it increases rapidly. Figure 1 shows typical combustion behaviour for a pre-mixed boiler where such changes in O_2 and CO levels are clearly highlighted.

There are less commonly encountered situations in
30   which significant changes in CO or O_2 level may occur without a major change in the concentration of the other species. Furthermore, "overgassing" may occur in which case fuel species or other partial combustion products such as H_2, CH_4 and heavier hydrocarbons can appear in the flue.
35   A simple, reliable means of rapidly detecting either a fall in O_2 content or a rise in CO level is therefore required, and if such means additionally allows the detection of

2

these other undesirable circumstances, this will confer
further advantage. Although the primary application
addressed here is that of a safety alarm activated in the
event of malfunction, it will also be clear that one or
5   more of these conditions may also be used to act as a
control parameter to ensure safe and efficient operation of
the combustion plant.

WO-A-93/08467 discloses a gas sensor for detecting
more than one gas but this requires separate sensing
10   elements.

In accordance with a first aspect of the present
invention, a method of detecting a predetermined alarm
condition in a combustion emission gas comprises exposing
to the gas a semiconductor gas sensor having a p-type
15   semiconducting material, the semiconducting material being
responsive both to a change in concentration of a reducing
gas in the surrounding atmosphere and to a change in
concentration of oxygen in the surrounding atmosphere to
exhibit a change in its electrical resistance; monitoring
20   the resistance; and outputting an alarm signal if the
resistance exceeds a predetermined value corresponding to
the alarm condition.

In accordance with a second aspect of the present
invention, a combustion emission gas alarm system comprises
25   a semiconductor gas sensor having a p-type semiconducting
material, the semiconducting material being responsive both
to a change in concentration of a reducing gas in the
surrounding atmosphere and to a change in concentration of
oxygen in the surrounding atmosphere to exhibit a change in
30   its electrical resistance; and apparatus for monitoring the
resistance of the semiconducting material and for issuing
an alarm signal if the resistance exceeds a predetermined
value corresponding to an alarm condition.

Thus we use a semiconductor material which will sense
35   oxygen, a reducing gas, or both in contrast to WO-A-
93/08467 where separate sensors are required.

3

The invention preferably utilizes mixed metal oxides of the first, second and/or third order transition metal series. However, it is believed that metal oxides or even other materials may exhibit the required properties.

5   Metal oxide semiconductor sensors typically operate at elevated temperatures somewhat higher than those encountered in small flues. Because of the demanding operating conditions, and their ability to respond to a number of parameters indicating potentially dangerous

10   situations, they represent a much more appropriate means of monitoring CO in this environment than other comparatively low cost sensors. For example, liquid electrolyte fuel cells are widely used in the industrial environment to detect dangerous levels of CO, but they are incapable of

15   surviving for any extended period in the atmospheric conditions of the flue due to their reliance on aqueous electrolytes. Furthermore, they generally only respond significantly to a single chemical species, so separate sensors would be required to measure CO and O_2. Catalytic

20   sensors, on the other hand, lack sensitivity to CO at the toxic levels of interest, are prone to poisoning of their catalysts and may give ambiguous or unreliable readings under changing oxygen levels.

       Since the flue gas application is a safety critical

25   one, where the lives of numerous persons adjacent to a malfunctioning boiler may be put in jeopardy, sensing technologies which offer fail safe operation are naturally preferred. The hot humid conditions within the flue, combined with the reducing nature of the flue gas and the

30   potential occurrence of poisons requires that the chosen technique should be robust against corrosion and breakage of sensor connections, or loss in sensitivity due to surface poisoning. Some semiconductor materials which are widely and successfully used in other gas sensing

35   applications are ill suited to this demanding role. The most commonly employed types are based on n-type tin oxide additionally containing precious metal catalyst additives

4

(for example those manufactured by Figaro and other companies), but these materials fail to meet the requirements of the application for a number of reasons;

(a) Although they can respond rapidly to changing oxygen levels as required, such responses may be wholly or partially irreversible due to bulk reduction of the oxide lattice. Such effects can occur even at comparatively moderate operating temperatures.

(b) They have a limited ability to function in the presence of species which can poison the surface sites governing the gas response. Moreover, such poisoning is not necessarily detectable other than by challenging the device with a calibration gas mixture, which is an impractical requirement in a domestic situation.

(c) The increased resistance which they provide on contact failure is in opposition to the reduced resistance output which occurs on detection of increased levels of CO or reduced oxygen content. As such, it is not immediately recognised by a simple signal processing system as indicative of a dangerous condition.

(d) They are particularly prone to interference from the effects of water vapour, which can swamp the signals derived from the species of interest.

In all these respects, the n-type tin oxide device does not fail safe and as such is unsuitable for the intended application.

Although much less widely used than n-type systems, p-type semiconductor materials are known in gas sensing applications (see, for example, Chapter 4 in "Sensor Materials" by P.T. Moseley & A.J. Crocker, IoP Publishing 1996). However, their specific advantages in the demanding combustion gas emission application have not previously been realised, appreciated or quantified.

We have found that p-type mixed metal oxide semiconducting sensors of the first, second and third order transition metal series are particularly well suited for combustion gas emission, particularly flue gas, detection,

5

for the following reasons;

(i)   They exhibit excellent chemical stability in wet reducing atmospheres, due to the particularly high formation energies of the oxides.

(ii) They are resilient to the effects of typical poisons such as mercaptans and silicone sealants since they do not rely upon the presence of precious metal catalysts to generate the gas sensitive signal.

(iii) They undergo a rapid and reversible increase in resistance in response to a decrease in oxygen and/or an increase in reducing gas, e.g. CO, content of the surrounding atmosphere. The relationship between the electrical resistance of such sensors, which is the response parameter used, and the carbon monoxide and oxygen concentrations in the test atmosphere follows a relationship of the form:

$$R_G = A[O_2]^{-1/x} + B[O_2]^{-1/x}[CO]^{1/2}$$

where :

R_G is the observed sensor resistance

$[O_2]$ is the oxygen concentration

$[CO]$ is the carbon monoxide concentration

A, B are constants which depend on the sensor resistance under reference conditions

x is a parameter which depends on the point defect chemistry of the oxide system. A typical value for x is 4.

There may be some departures to this relationship in cases where the flue temperatures are at the upper end of the range 40-200°C, resulting in the volume percent of water in the atmosphere increasing dramatically. Notwithstanding this, the overriding importance of this relationship is that it means that each undesirable condition (increased CO or decreased O_2) causes a change in resistance of the same sense which can be easily monitored.

(iv) They also possess a significant reversible response to other reducing species of interest.

(v) Connection faults giving rise to an apparent resistance rise can be identified as a dangerous state by a simple alarm system since the target gases will also produce a resistance increase.

Although a wide range of p-type materials are in principle suitable for such applications, the following examples are based on tests performed using standard commercial devices marketed for CO monitoring (Capteur sensor CAP07, City Technology Ltd). This design employs p-type oxides of the Cr-Ti-Mn-O system, for example as described in WO-A-01/88517, EP-A-0940673, EP-A-1135336 and EP-A-0656111. Other materials include CuO with 10% TiO_2 and CoO with 5% TiO_2.

An example of a system and method for detecting a predetermined alarm condition in a combustion emission gas will now be described with reference to the accompanying drawings, in which:-

Figure 1 illustrates typical combustion curves for a pre-mixed boiler;

Figure 2 illustrates the variation in sensor resistance with carbon monoxide concentration;

Figure 3 illustrates the variation in sensor resistance with oxygen concentration;

Figure 4 illustrates the dependency of sensor resistance on carbon monoxide and oxygen concentrations for a number of different sensors;

Figure 5 illustrates the response of the sensor to a variety of different gases in 5% oxygen and 24% relative humidity;

Figure 6 illustrates the behaviour of three sensors in a flue atmosphere together with an example of the response of an electrochemical CO sensor in a cooled extracted sample of the gas;

Figure 7 is similar to Figure 6 but in which a cooled extracted sample of the gas has been supplied to an electrochemical oxygen sensor;

Figure 8 is a block diagram of the system;

Figure 9 illustrates how resistance of the sensor is determined; and,

Figure 10 illustrates the response of various p-type MMOS sensors in two carbon monoxide/oxygen gases.

In this example, a combustion emission gas sensor is based on the use of a p-type oxide of the Cr-Ti-O system. The use of such materials in sensors is known and will be briefly described.

The sensor takes the form of a highly porous oxide layer, which is printed down onto an alumina chip. The electrodes are co-planar and located at the oxide/chip interface. A heater track is present on the backside of the chip to ensure the sensor runs "hot". This is a necessary requirement as both the interference from humidity is minimized and the speed of response is increased. MMOS sensors do not normally discriminate between different target gases. As such, considerable care is taken to ensure the microstructure of the oxide, its thickness and its running temperature are optimized to improve selectivity. In addition, selectivity is further enhanced through the use of catalytic additives to the oxide, protective coatings and various types of activated-carbon filters and on-chip catalytic oxide layers. In this example, the porous Cr-Ti-O oxide layer is coated with a catalytic oxide layer.

As can be seen in Figure 8, the sensor 1 is connected to a heater driver bridge circuit 2 for controlling the sensor heater. An EEPROM (not shown) within the sensor 1 is connected to a microprocessor 3 while the output from the sensor 1 is connected to a simple amplification circuit 4. The EEPROM contains heater control data corresponding to the calibration temperature of the sensor. The circuit 2 and the circuit 4 are powered from a power supply 5. The

8

processor 3 generates an output signal which, in this case, is fed to an alarm which may be a visual or audible alarm 6. In other cases, this signal could instead or additionally be fed to a control system of a boiler or
5   other equipment generating the combustion emission gas which is being monitored.

As explained above, the sensor resistance increases with both increasing CO concentration (Figure 2) and decreasing O_2 concentration (Figure 3). Thus, whenever the
10   air supply drops or when there is incomplete combustion for other reasons, the sensor will detect the condition as a result of this combined effect. Figure 4 demonstrates this for a range of sensors exposed to various CO/O_2 combinations. It can be seen that the sensor resistance in
15   200ppm CO at 10%O_2 is comparable to that in 100ppm CO at 5% O_2 which in turn is comparable to that at <50ppm at 2.5% O_2. The sensors in this example were carefully selected from a standard batch, representing the two extremes in performance, i.e. at both ends of the 95% confidence range.
20   In addition to the sensor 1 being alert to the presence of CO and varying O_2 concentrations, it will also respond to the presence of other relevant gases, such as H_2, CH_4, and other heavier hydrocarbon fuels. Figure 5 shows typical responses to these gases over a range of
25   different concentrations. The error bars represent the full range of responses for 10 sensors. A continuous atmosphere of 5% O_2 was maintained in this test to replicate conditions in a boiler flue whose gas is being detected.
30   If the sensor 1 is to be considered for use in boiler flue applications, it is important that its performance should not degrade while continuously operated over a time period commensurate with the life of the boiler or an acceptable maintenance interval. Longevity data is not as
35   yet available for sensors operated within the flue. However, the performance of similar devices operated under typical domestic conditions (for which application the

9

sensor was originally designed) meets the 1 year test
requirements of the UL2034 standard for domestic fire
detection applications.

5   Figures 6 and 7 show the performance of 3 p-type
sensors in the flue of a condensing gas furnace. The
sensors are based on sensing layers employing the Cr-Ti-O
system and were set up to a resistance of 50 kohms in clean
air at 50% relative humidity. At this resistance, the
sensors are running at about 480-500°C. The sensors were
10   installed in a vertical tube ducting the flue gases away
from the heat exchange coils. The temperature of the flue
gases at this point was 40°C. As a cross-check, a sample
of the flue gas was extracted and cooled and then drawn
across an electrochemical CO sensor (3F/F, City Technology
15   Ltd) and an electrochemical O_2 sensor (2FO, City Technology
Ltd). To create an unsafe condition, the vertical tube was
restricted in stages by means of a sliding plate. It can
be seen from Figures 6 and 7 that the p-type sensors
respond to both a reduction in oxygen level and an increase
20   in CO level. The combined effects of these two responses
gives rise to a very large signal from the p-type sensors
which could readily be used in conjunction with a variety
of simple signal processing means to alert users of these
potentially dangerous conditions.

25   It will be seen from the above discussion that alarm
conditions caused by an increase in a toxic gas such as
carbon monoxide and decrease in oxygen both cause an
increase in resistance and this change in resistance is
monitored by the processor 3 which will compare the
30   monitored resistance with a predetermined threshold set
such that if the threshold is exceeded, this indicates a
dangerous or alarm condition. In that situation, the alarm
6 is activated.

As explained above, the resistance rises proportional
35   to the amount of carbon monoxide (or oxygen) present and a
typical resistance range is 50KΩ (base line value with no
gas present/clean air) to 150KΩ. If the sensor is exposed

to a sufficiently high current, polarization of the sensor material may occur. This requires that the sensor be measured using a low, <0.1V reference voltage. This is achieved by using a simple potential divider as shown in
5   Figure 9.

A voltage reference is generated and appropriate resistors 11,12 chosen to generate a voltage across the sensor of 0.1V or less. The sensing element 13 of the sensor is connected in series with a 50KΩ resistor 14 with
10   the 0.1V signal applied across both resistors. The output from the sensor is then taken from the point 15 between the two resistors. This output voltage is amplified to a sensible value, typically a gain of about 100, using the amplification circuit 4 to bring the signal with the range
15   of the analog-to-digital converter input of the microprocessor 3.

The sensor described above uses a Cr-Ti-O material, for example Cr-Ti-Mn-O. Other suitable materials include TiO_2 doped CoO and CuO.
20

Examples

Sensors from three different p-type gas-sensitive oxide systems, Co-O (J R Stetter, J Colloid Interface Science, 65 (1978) 432, and E M Logothetis et al, Appl Phys
25   Letters, 26 (1975) 209), Cu-O (J Gentry and T A Jones, Sensors and Actuators, 4 (1983) 581-586) and Cr-Ti-Mn-O (EP-A-1135336) which display p-type behaviour were made up. For each system, the Cr-Ti-O oxide layer in the standard City Technology CO product, Cap07, was replaced with a
30   layer comprised of one of its oxides. For Co-O and Cu-O, TiO_2-doped compositions, CoO-5wt%TiO2 and CuO-10wt%TiO2 were used. Prior to being made into a screen-printable ink, the oxide powders were either sieved through a 32 micron sieve (Cr-Ti-Mn-O) or a 125 micron sieve (Co-Ti-O,
35   Cu-Ti-O). The specific temperatures of sensor operation were 450°C for both the Co-Ti-O and Cu-Ti-O examples and 400°C for the Cr-Ti-Mn-O example, respectively.

11

The sensors were initially exposed to air at 50% relative humidity (RH), followed by sn exposure to 1031ppm CO in 21% O_2 for 15 minutes, a clean-up exposure in 50% RH air, an exposure to 1025ppm CO in 1.5% O_2, and a final clean-up exposure in air at 50% RH. The results shown in Figure 10 demonstrate that these materials respond to 1031ppm CO but in addition, the signal is further increased when exposed to a similar CO level but with a greatly reduced O_2 level. It is therefore evident that these systems are sensitive to atmospheric conditions in which the CO level increases and/or the O_2 level decreases.

12

CLAIMS

1.   A method of detecting a predetermined alarm condition in a combustion emission gas, the method comprising exposing to the gas a semiconductor gas sensor having a p-type semiconducting material, the semiconducting material being responsive both to a change in concentration of a reducing gas in the surrounding atmosphere and to a change in concentration of oxygen in the surrounding atmosphere to exhibit a change in its electrical resistance; monitoring the resistance; and outputting an alarm signal if the resistance exceeds a predetermined value corresponding to the alarm condition.

2.   A method according to claim 1, wherein the reducing gas is one of CO, H_2, CH_4 and higher hydrocarbons.

3.   A method according to claim 1 or claim 2, wherein the electrical resistance of the semiconductor gas sensor is related to the concentrations of oxygen and carbon monoxide in the surrounding atmosphere over at least a range of atmospheric compositions via an expression of the form:

$$R_G = A[O_2]^{-1/x} + B[O_2]^{-1/x}[CO]^{1/2}$$

where :

R_G is the observed sensor resistance

$[O_2]$ is the oxygen concentration

$[CO]$ is the carbon monoxide concentration

A, B are constants which depend on the sensor resistance under reference conditions

x is a parameter which depends on the point defect chemistry of the oxide system.

4.   A method according to any of the preceding claims, wherein the p-type material comprises a metal oxide.

5.   A method according to any of claims 1 to 3, wherein the p-type material comprises a mixed metal oxide.

6.   A method according to claim 4 or claim 5, wherein the metal is of the first, second and/or third order transition metal series.

7. A method according to claim 6, wherein the
semiconductor material comprises a p-type oxide of the Cr-
Ti-O system.

8. A method according to claim 6, wherein the
5 semiconductor material comprises a p-type Cr-Ti-Mn-O
system, CuO with TiO_2 or CoO with TiO_2.

9. A method according to any of the preceding claims,
wherein the combustion emission gas is a flue gas.

10. A combustion emission gas alarm system comprising a
10 semiconductor gas sensor having a p-type semiconducting
material, the semiconducting material being responsive both
to a change in concentration of a reducing gas in the
surrounding atmosphere and to a change in concentration of
oxygen in the surrounding atmosphere to exhibit a change in
15 its electrical resistance; and apparatus for monitoring the
resistance of the semiconducting material and for issuing
an alarm signal if the resistance exceeds a predetermined
value corresponding to an alarm condition.

11. A system according to claim 10, wherein the electrical
20 resistance of the semiconductor gas sensor is related to
the concentrations of oxygen and carbon monoxide in the
surrounding atmosphere over at least a range of atmospheric
compositions via an expression of the form:

$$R_G = A[O_2]^{-1/x} + B[O_2]^{-1/x}[CO]^{1/2}$$

25   where :

R_G is the observed sensor resistance

$[O_2]$ is the oxygen concentration

$[CO]$ is the carbon monoxide concentration

A, B are constants which depend on the
30   sensor   resistance   under   reference
conditions

x is a parameter which depends on the point
defect chemistry of the oxide system.

12. A system according to claim 10 or claim 11, wherein
35 the p-type material comprises a metal oxide.

13. A system according to claim 10 or claim 11, wherein
the p-type material comprises a mixed metal oxide.

14.   A system according to claim 12 or claim 13, wherein the metal is of the first, second and/or third order transition metal series.

15.   A system according to claim 13 or claim 14, wherein the semiconductor material comprises a p-type oxide of the Cr-Ti-O system.

16.   A system according to claim 13 or claim 14, wherein the semiconductor material comprises a p-type CuO with TiO_2 or CoO with TiO_2.

17.   A system according to any of claims 10 to 16 mounted to or adjacent to a flue gas outlet so as to expose the sensor to a gas flue.
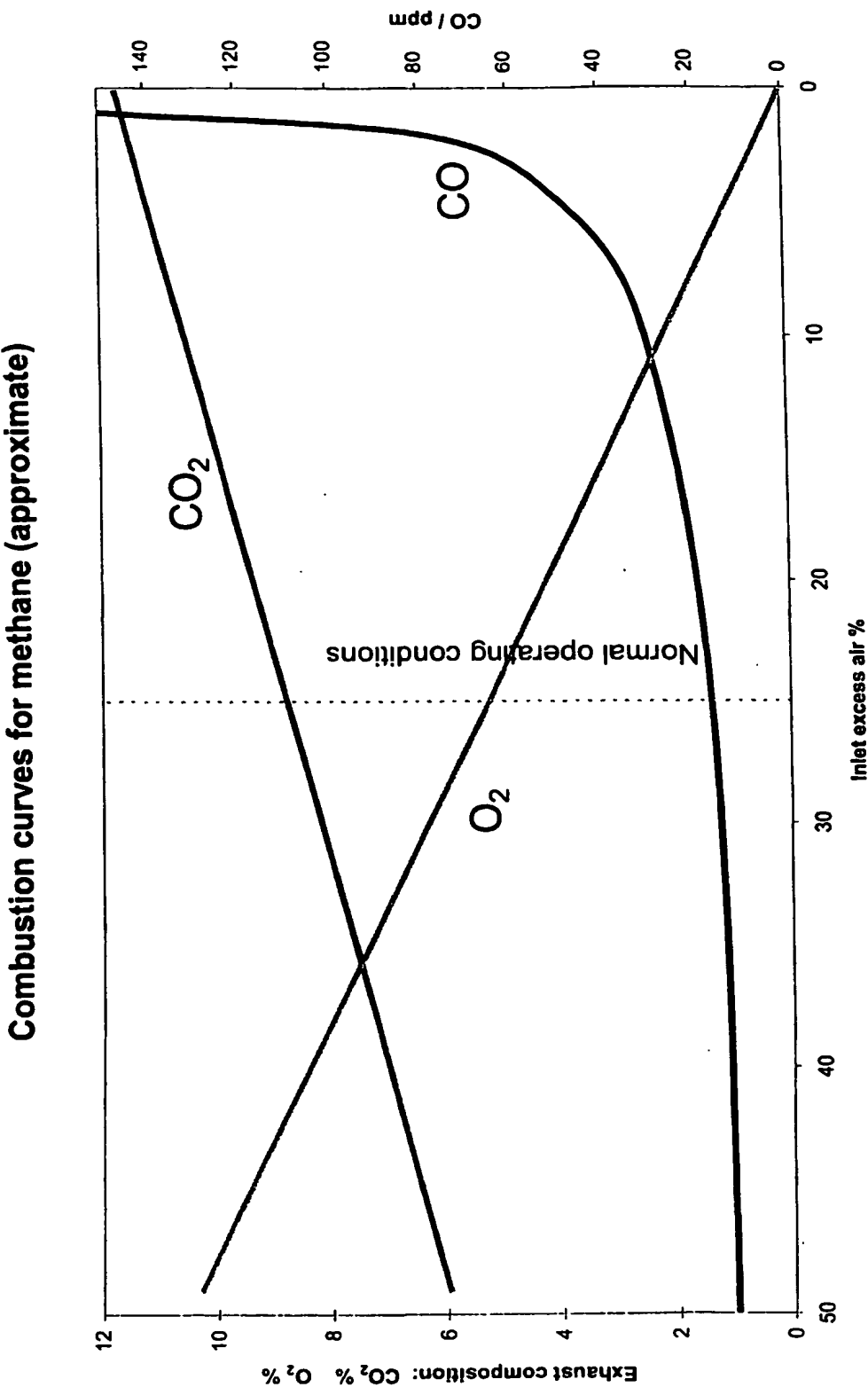
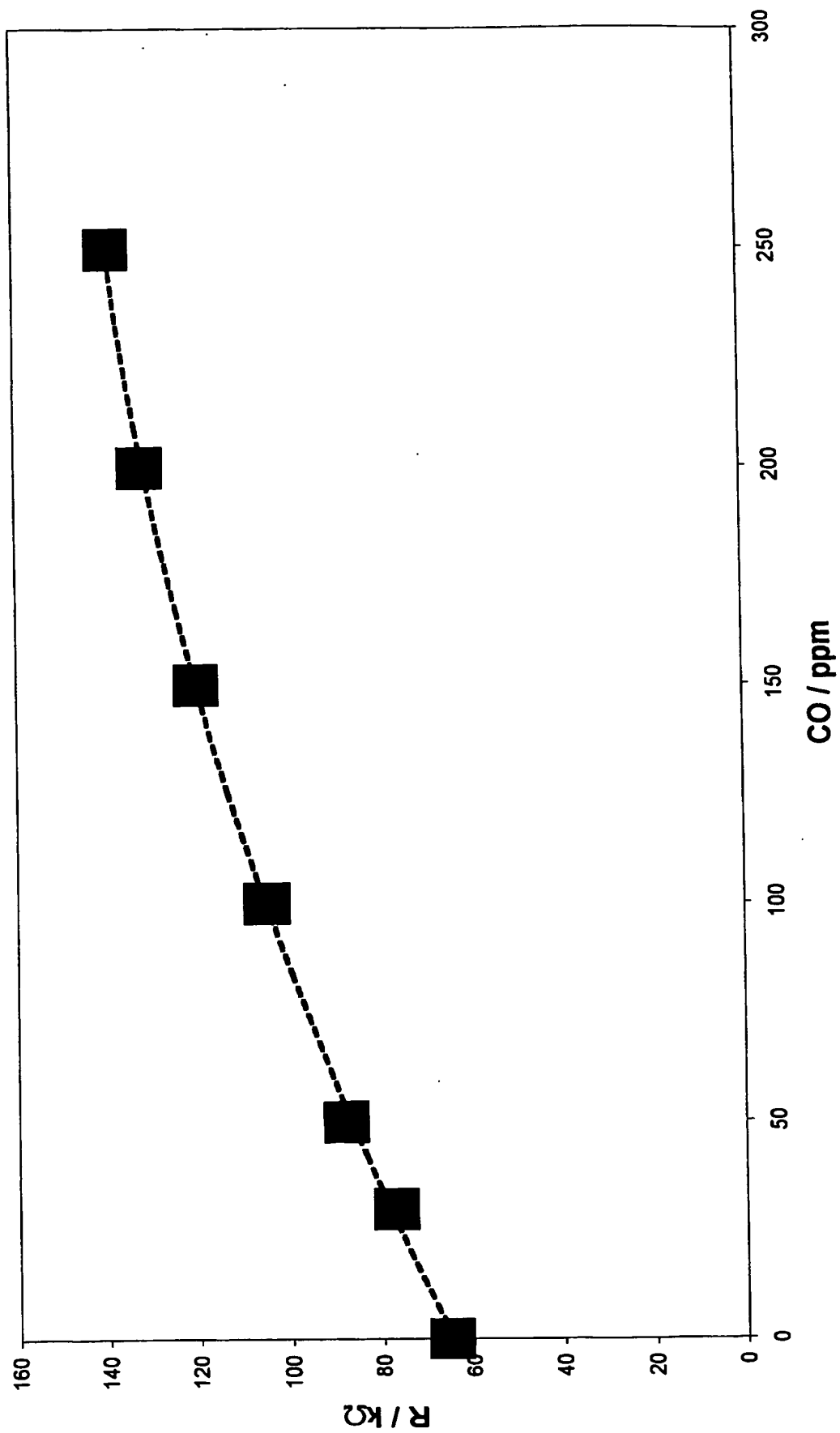Figure 1 : Typical combustion curves for a pre-mixed boiler
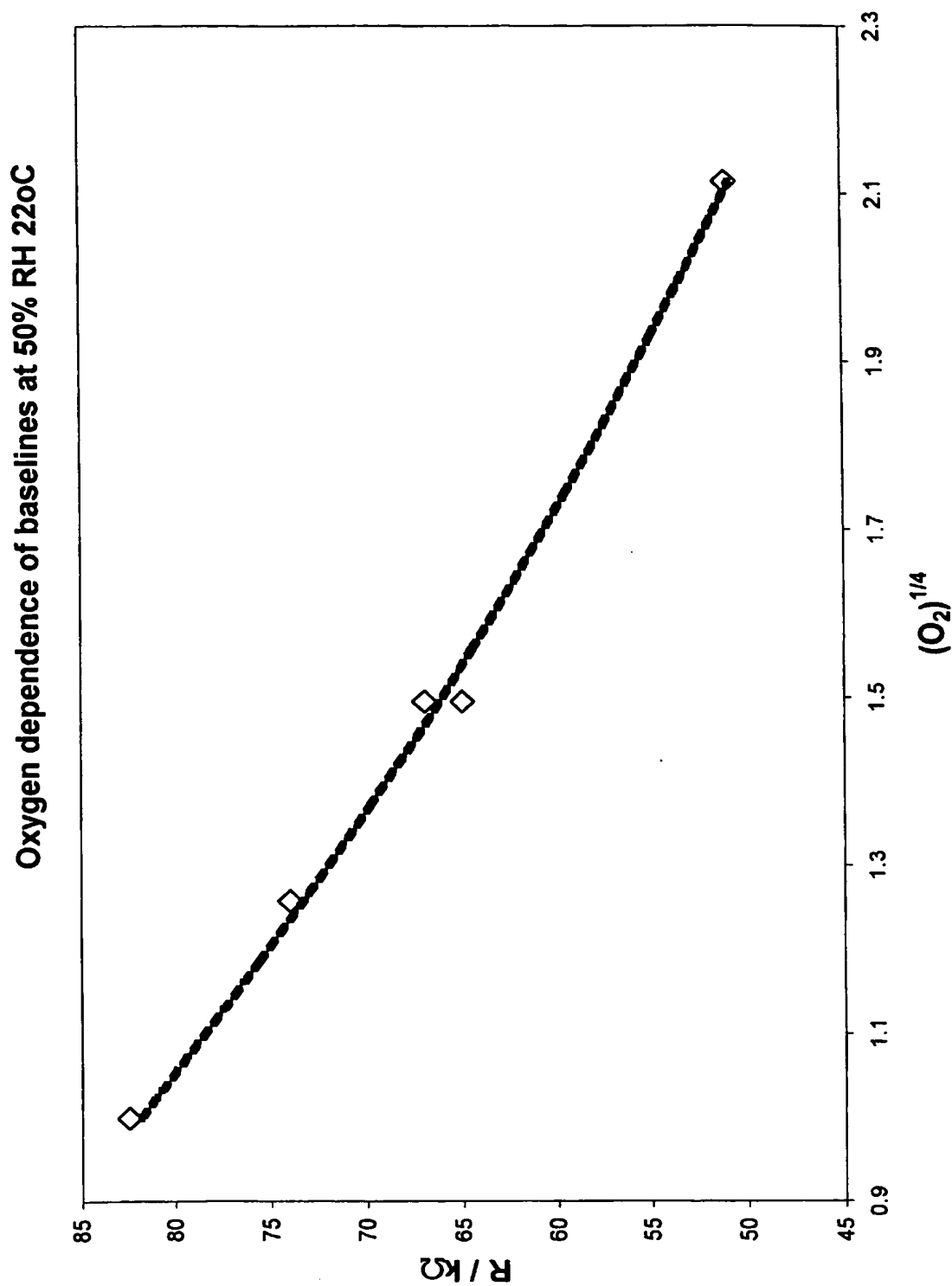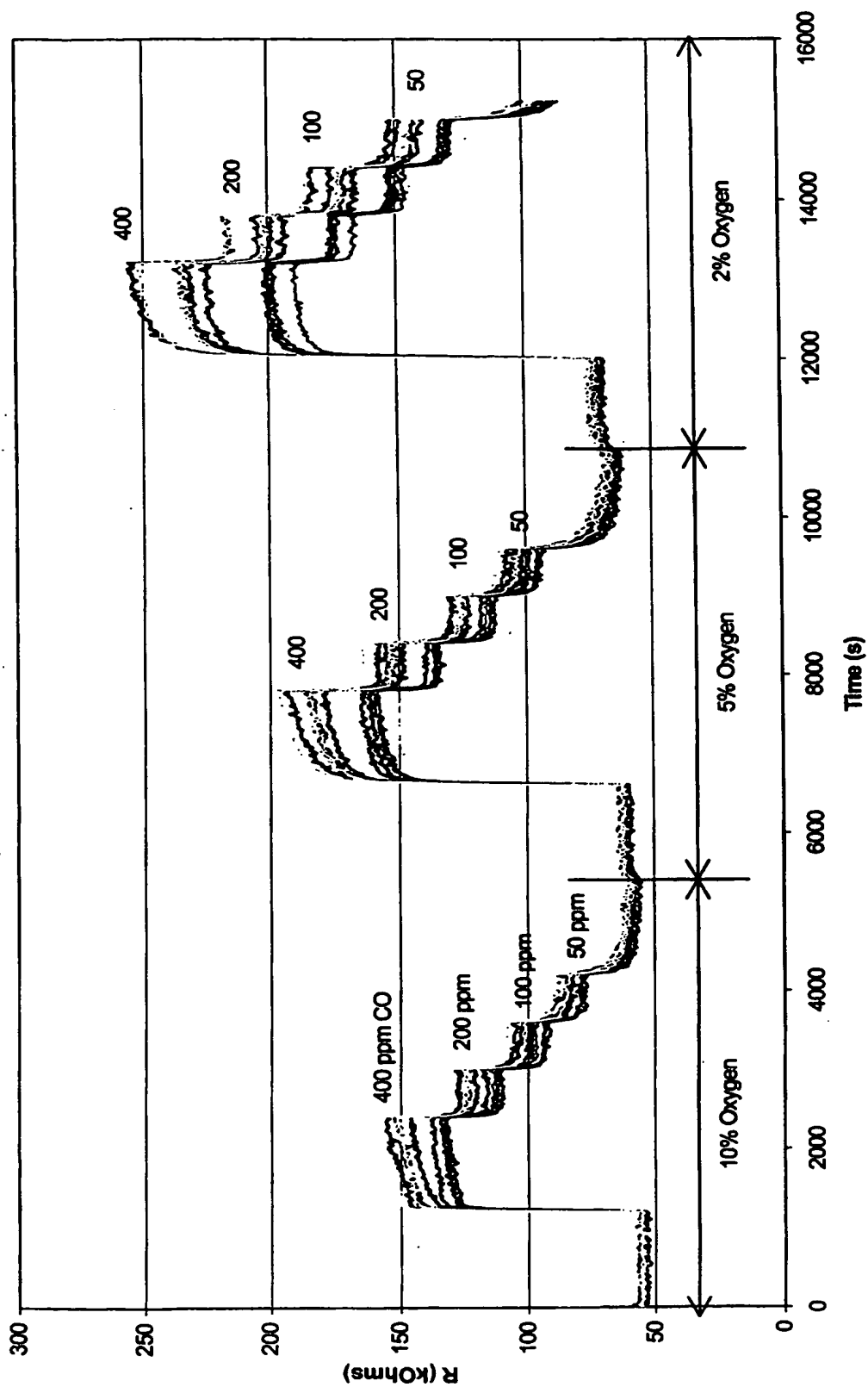
FIG. 2

FIG. 3

Figure 4 : Dependency of sensor resistance on CO and O₂ concentrations

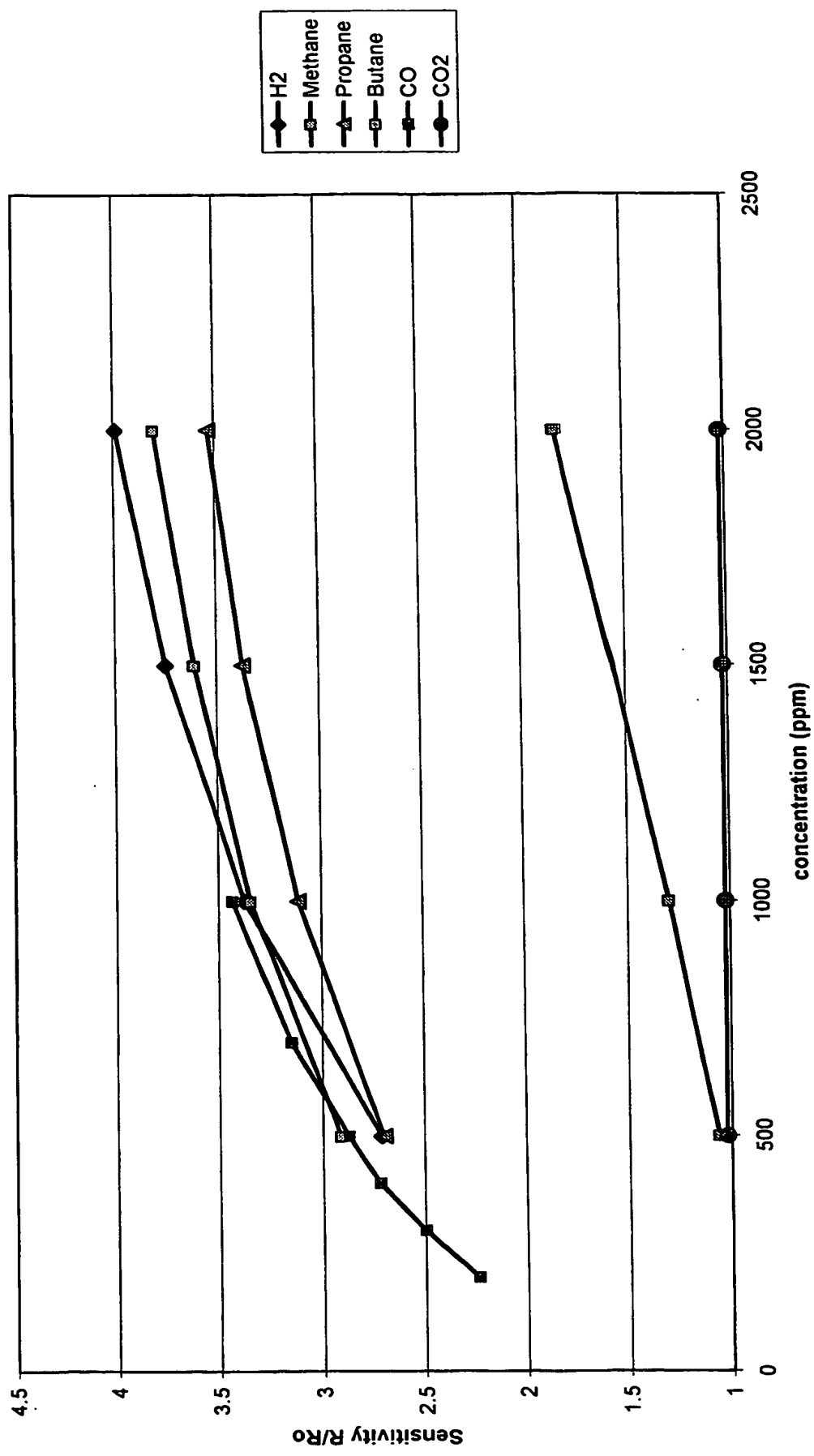Sensitivity of NG sensors exposed to varying concentrations of gases in an atmosphere of 5% O2 and 24% RH
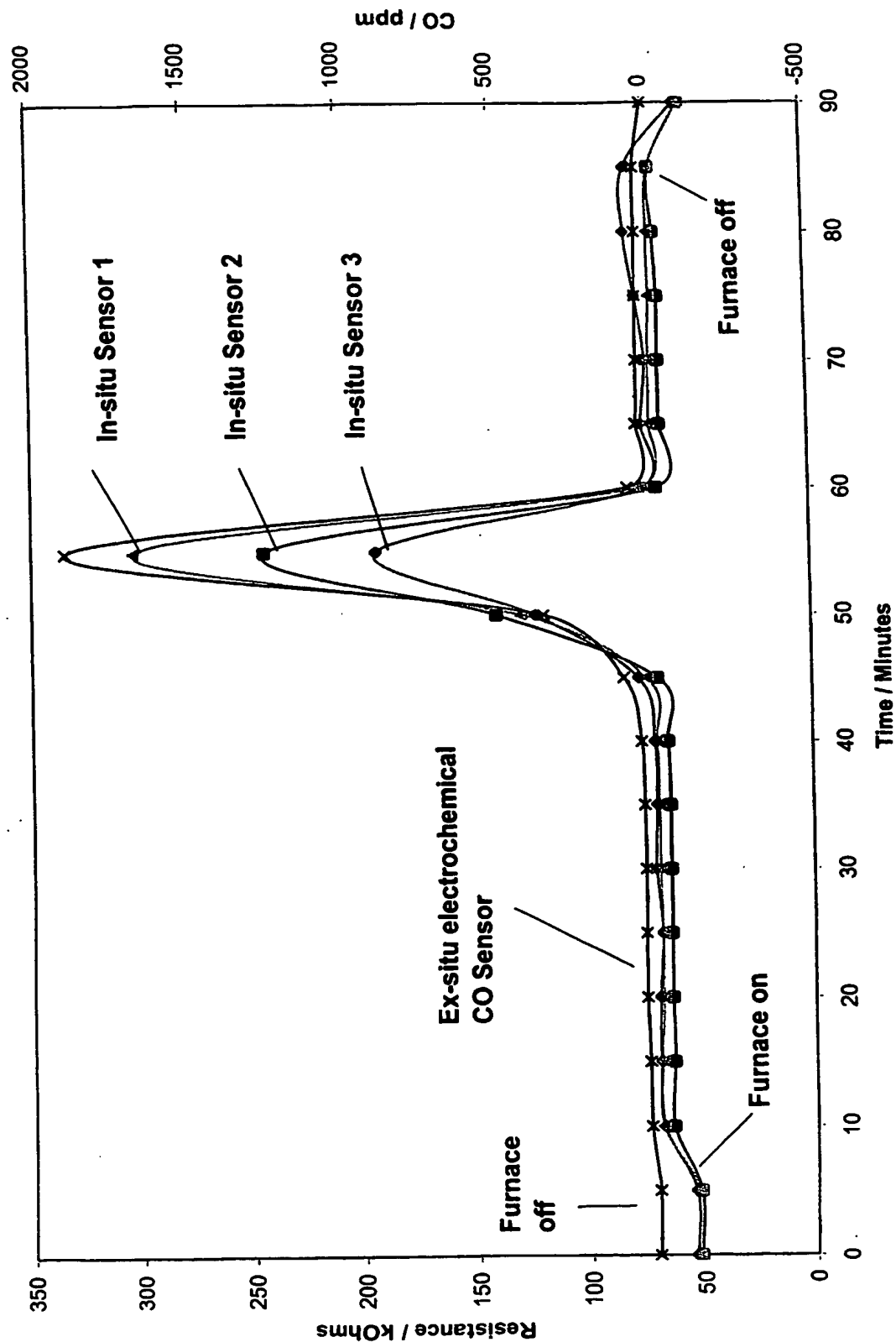
FIG. 5

Figure 6: Behaviour of 3 p-type MMOS sensors in a flue atmosphere. The response of an electrochemical CO sensor in a cooled extracted sample of the gas is also shown.
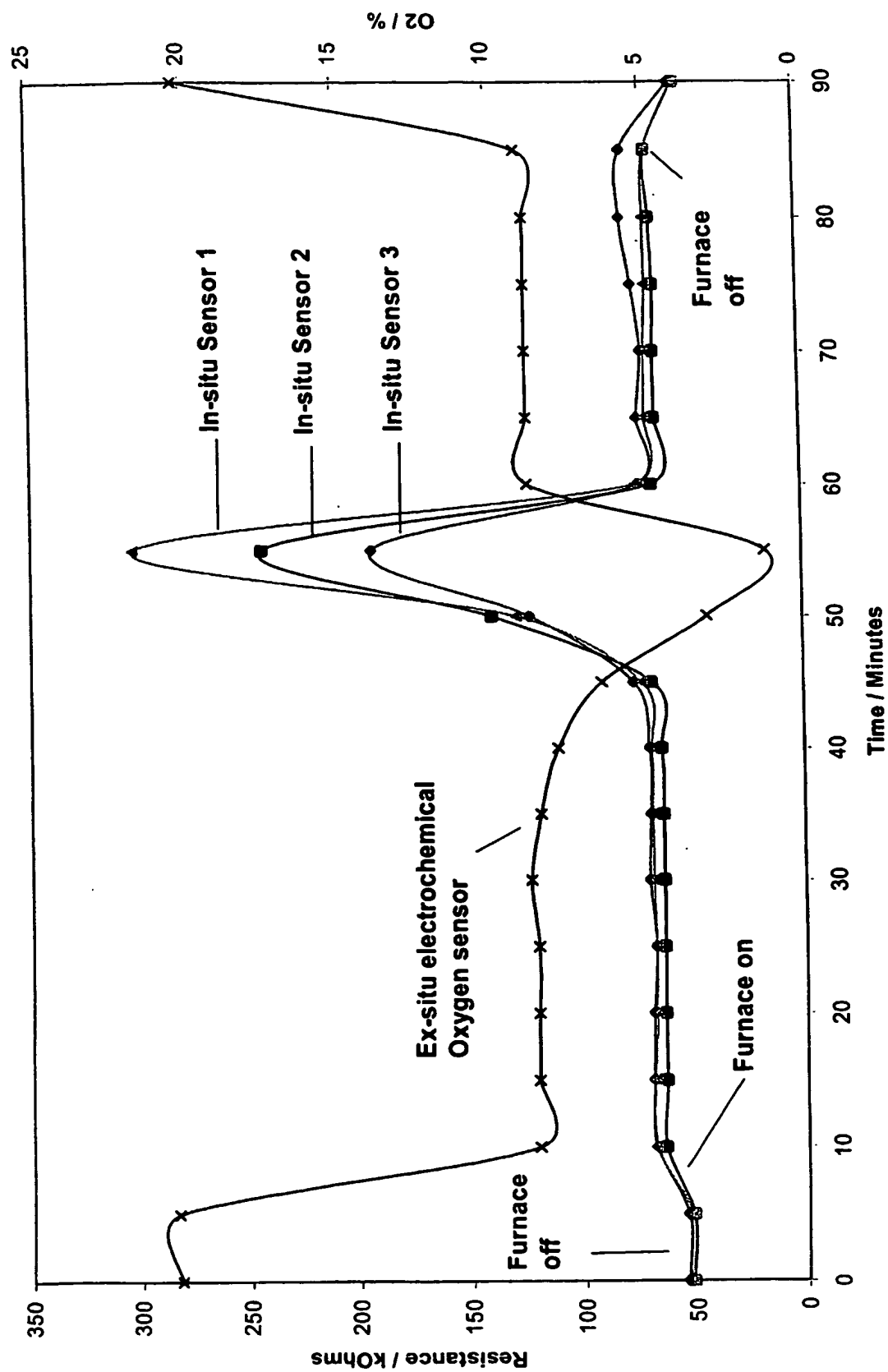
Figure 7: Behaviour of 3 p-type MMOS sensors in a flue atmosphere. The response of an electrochemical O_2 sensor in a cooled extracted sample of the gas is also shown.

ALARM — 6

PROCESSOR — 3

HEATER DRIVER
BRIDGE CIRCUIT — 2

CGS — 1

SIGNAL AMPLIFICATION — 4

POWER SUPPLY — 5

FIG. 8

+V   0.1V

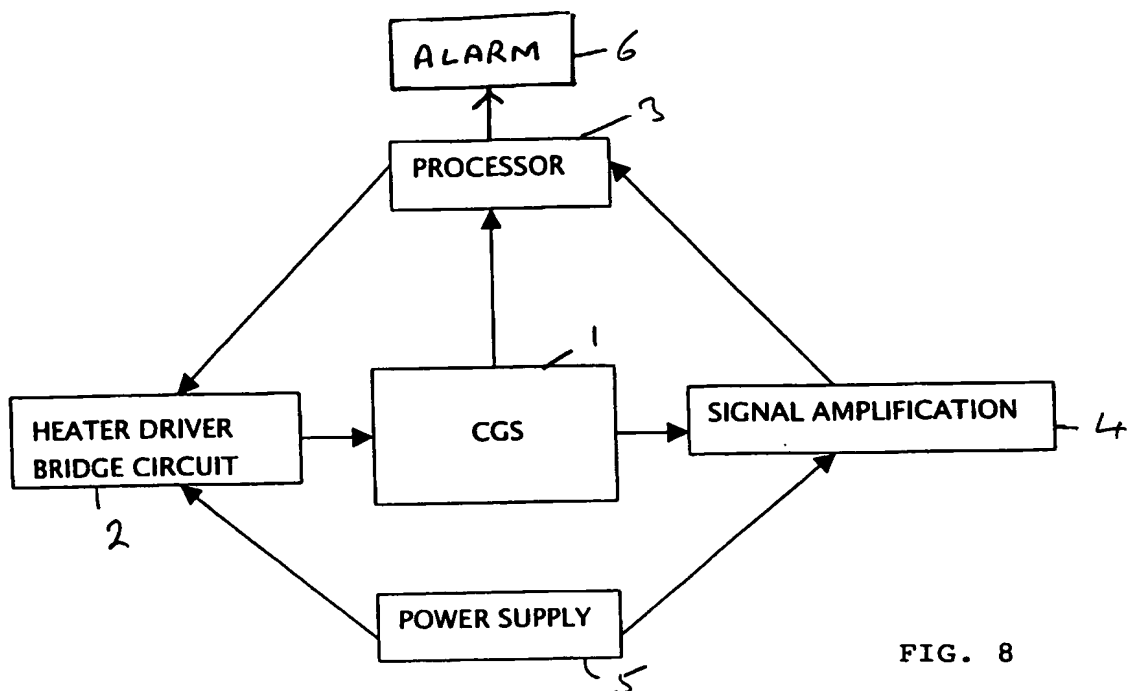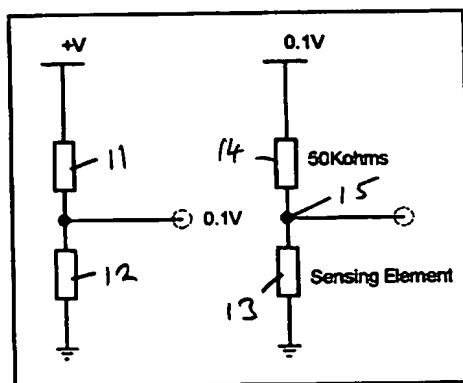11   14 — 50Kohms

0.1V   15

12   Sensing Element — 13

FIG. 9

Response of various p-type MMOS sensors in 2 Carbon Monoxide/Oxygen gases
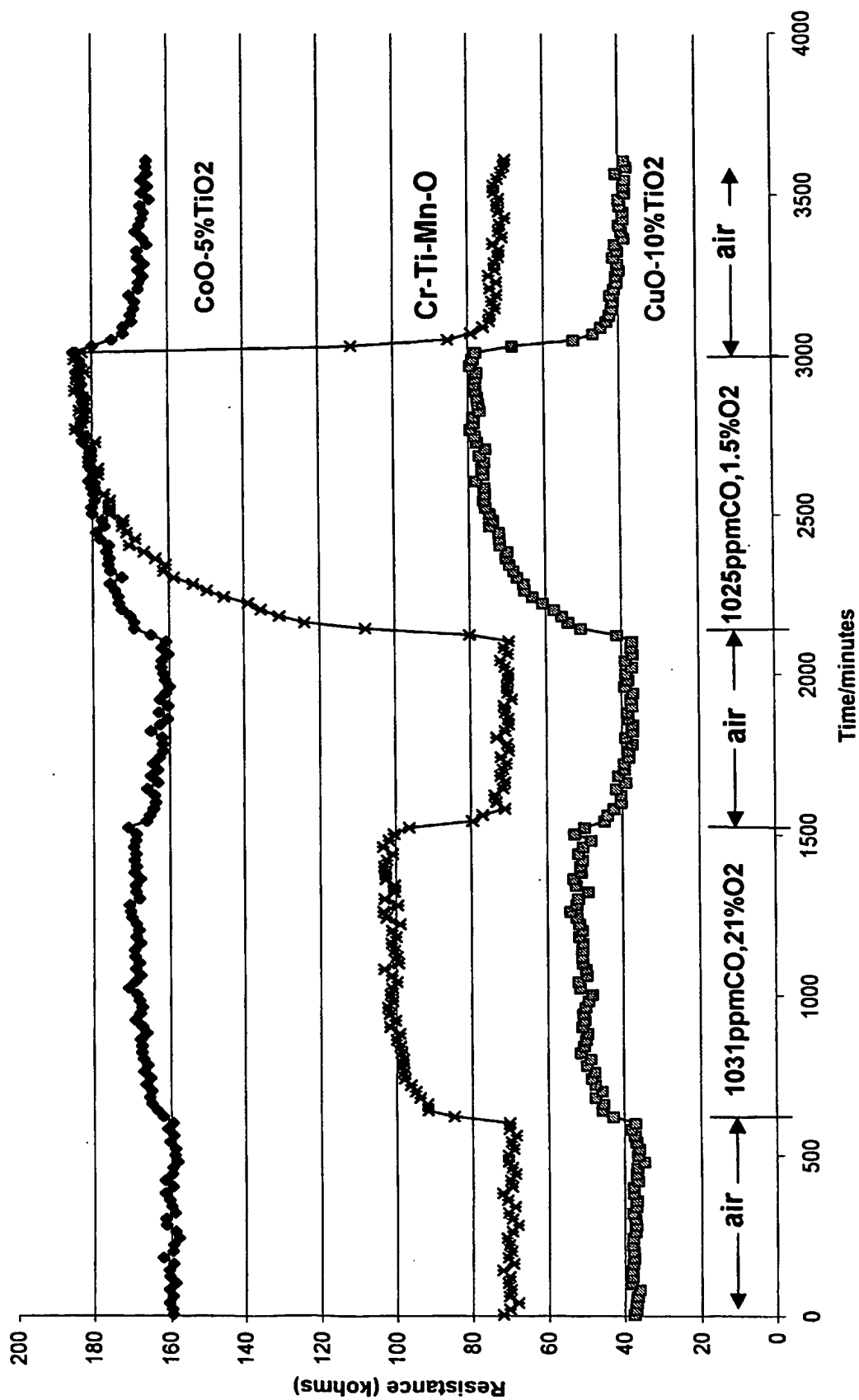
FIG. 10

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   G01N33/00   G01N27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 93 08467 A (CAPTEUR SENSORS & ANALYSERS) 29 April 1993 (1993-04-29) page 4, line 1 – line 28 page 5, line 14 – line 26 page 6, line 21 – line 30 page 7, line 18 – line 31 page 8, line 14 – line 18 page 10, line 21 – line 24 page 11, line 11 –page 12, line 2 page 12, line 28 –page 13, line 14; figures 2D,3A,3E ---	1,2,4-7, 9,10, 12-15,17
Y	US 6 046 054 A (DAWSON DARRYL HIRST ET AL) 4 April 2000 (2000-04-04) column 1, line 61 – line 65; tables 3,4 --- -/--	1,2,4-7, 9,10, 12-15,17

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 January 2004	30/01/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Joyce, D

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01 38867 A (CAPTEUR SENSORS ANS ANALYSERS ;KING CHARLES EDMUND (GB); SMITH PET) 31 May 2001 (2001-05-31) page 5; table 1	8
A	EP 1 008 847 A (SIEMENS AG) 14 June 2000 (2000-06-14) claim 6	8,16
A	EP 1 041 039 A (IMRA EUROP SA) 4 October 2000 (2000-10-04) paragraph '0009!	16
A	WO 95 00836 A (CAPTEUR SENSORS & ANALYSERS ;MCGEEHIN PETER (GB); MOSELEY PATRICK) 5 January 1995 (1995-01-05) cited in the application the whole document	1-9

INTERNATIONAL SEARCH REPORT

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9308467	A	29-04-1993	EP	0609316 A1	10-08-1994
			WO	9308467 A1	29-04-1993
US 6046054	A	04-04-2000	AU	6976594 A	17-01-1995
			CA	2142696 A1	05-01-1995
			DE	69422892 D1	09-03-2000
			DE	69422892 T2	05-10-2000
			EP	0656111 A1	07-06-1995
			EP	0940673 A2	08-09-1999
			WO	9500836 A1	05-01-1995
			GB	2285689 A	19-07-1995
			JP	8500447 T	16-01-1996
			JP	2003315300 A	06-11-2003
WO 0138867	A	31-05-2001	CA	2392434 A1	31-05-2001
			EP	1236041 A2	04-09-2002
			WO	0138867 A1	31-05-2001
			JP	2003515168 T	22-04-2003
EP 1008847	A	14-06-2000	DE	19856369 A1	15-06-2000
			EP	1008847 A2	14-06-2000
EP 1041039	A	04-10-2000	FR	2791661 A1	06-10-2000
			EP	1041039 A1	04-10-2000
			JP	2000283941 A	13-10-2000
WO 9500836	A	05-01-1995	AU	6976594 A	17-01-1995
			CA	2142696 A1	05-01-1995
			DE	69422892 D1	09-03-2000
			DE	69422892 T2	05-10-2000
			EP	0656111 A1	07-06-1995
			EP	0940673 A2	08-09-1999
			WO	9500836 A1	05-01-1995
			GB	2285689 A	19-07-1995
			JP	8500447 T	16-01-1996
			JP	2003315300 A	06-11-2003
			US	6046054 A	04-04-2000